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Monitoring at Chemical Agent Disposal Facilities—*Summary*

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Background

Under the direction of the U.S. Army's Chemical Materials Agency (CMA) the nation is destroying its chemical weapons stockpile. Destruction of these weapons has been mandated by Congress. In addition, the Chemical Weapons Treaty, which the U.S Senate ratified in 1997, requires the entire stockpile to be destroyed by 2012. To date, just over a third of the chemical agent in the original stockpile has been destroyed. It is likely that disposal operations will not be completed until 2012 or later. Over the past several years, the Army has requested several studies from the NRC to assist with the stockpile destruction. This study was requested to advise the CMA about the status of analytical instrumentation technology and systems suitable for monitoring airborne chemical warfare agents at chemical weapons disposal and storage facilities. The report presents an assessment of current monitoring systems used for airborne agent detection at CMA facilities and of the applicability and availability of innovative new technologies. It also provides a review of how new and more demanding regulatory requirements for airborne agent monitoring would affect the effectiveness of the CMA's current agent monitoring procedures, and whether new measurement technologies that would enhance current agent monitoring capabilities are available and could be effectively incorporated into the CMA's overall chemical agent monitoring strategies.

Chemical Agent Monitoring Challenge

In order to protect its workforce as well as both the general public and the environment near its facilities, the CMA monitors airborne chemical agents at exceedingly low levels in near-real-time (NRT), i.e. intervals of less than 15 minutes. The purpose of this monitoring is to warn workers if unexpected levels of agent have penetrated areas in which protective gear is normally not required. Exhaust emissions in the pollution abatement system and the exhaust stack are also monitored for agents by NRT instruments at the source emission limits (SELs) that are levels only modestly higher than those acceptable for the ambient air in the facility.

In addition, using sample collection and analysis techniques, historical monitoring is performed within the facility in accordance with new airborne exposure limits (AEL) promulgated by the Center for Disease Control (CDC) in 2003 and 2004 to ensure that the workers are not exposed to very low but persistent levels of agent. These same sampling and laboratory analysis systems are used as confirmation monitors to determine if adjacent NRT monitor alarms are actually caused by a chemical agent or another pollutant. Finally, the sampling and analysis method is also used at CMA facility perimeters to monitor at extremely low agent levels based on the new CDC recommendations. Such monitoring is intended to ensure that no significant level of agent migrates beyond a CMA facility and affects the nearby public or environment.

Findings and Recommendations

Adoption of new AEL The need to detect very low chemical agent concentrations within air masses that may also contain much higher levels of other industrial and environmental contaminants that can interfere with chemical agent detection makes the CMA's monitoring tasks very challenging. Nevertheless, the CDC's newly promulgated AEL, the short-term exposure limit (STEL), is an appropriate basis for NRT monitoring at CMA facilities, since it ensures worker protection. The Army should continue to use short-term exposure limits (STELs) as the basis for near-real-time monitoring.

Current airborne agent monitoring systems Frequent NRT false-positive alarms have been a persistent problem. The Army has made progress in reducing NRT false positives, however, this type of false-positive alarm will likely continue to be a problem, particularly for the nerve agent VX. Furthermore, an increased frequency of false positives may be experienced for historical monitoring sample-collection-and-laboratory-analysis systems as the CMA implements the 2003/2004 AEL levels for historical monitoring of the workplace and facility boundary. Despite some problems with false-positive measurements, the current NRT monitoring and the monitoring technology for sampling and laboratory analysis appear to provide sufficient airborne agent monitoring capability to afford adequate protection to workers, the general public, and the environment. Given that the disposal operations will be ongoing for some years, at least until 2012 and perhaps beyond. The CMA should consider a wider range of incremental improvements to its current monitoring systems to allow them to monitor more effectively at the CDC's 2003/2004 AELs.

The CMA has historically set the NRT alarm levels at some fraction of the relevant AEL or SEL, with the goal of ensuring a statistical alarm response rate of 95 percent or better when agent is present at the AEL or SEL. Neither the CMA's plans to possibly set alarm levels at 1.0 AEL/SEL nor the inclination of state regulators to specify alarm levels of 0.2 AEL may be optimal. The Army should consider continuing to use alarm levels that ensure that all properly operated and maintained NRT monitors at a given site have at least a 95 percent probability of sounding an alarm any time the true agent concentration in an area being monitored exceeds 1.00 STEL. This can often be achieved with an alarm level of ~0.5 AEL/SEL, and such a setting also will tend to reduce false-positive alarms without greatly enhancing the probability of false-negative measurements.

Advanced chemical agent monitoring technology Two vibrational spectroscopy technologies—Fourier transform infrared (FT-IR) spectroscopy, employed in either an open-path or a folded multi-pass gas cell configuration, and surface-enhanced Raman scattering (SERS)were evaluated as possible agent monitor candidates. FT-IR spectroscopy will likely have limited utility because its limited sensitivity for the relevant chemical agents makes real-time detection at STEL or lower AELs problematic. Likewise, SERS is not likely to allow real-time agent detection at STEL levels and does not promise significant advantages over current NRT monitors.

Chemical ionization mass spectrometry (CIMS) is a highly sensitive trace gas detection technique that is potentially capable of measuring the stockpiled chemical agents at concentrations well below STEL levels in real time. The Army should investigate whether current commercial CIMS instrumentation could be immediately used to detect chemical agents at the immediately dangerous to life and health (IDLH) or lower limits in realtime. The use of negative ions as a precursor should be investigated to improve selectivity. Adaptation of one of the current research-grade atmospheric field instruments for real-time detection between the STEL and the GPL for each relevant agent also should be considered.

Chemical sensor arrays are an innovative and fast developing trace chemical measurement approach that might soon be useful in detecting agents at the relatively high IDHL limit. The development time required for these sensor arrays to work reliably at the STEL or lower AELs is probably too long to impact the CMA's chemical weapons disposal program. Since the federal government is currently the only obvious customer for chemical agent detection at STEL or lower levels, the commercial development of sensors with this capability is unlikely without direct federal support.

Chemical agent monitoring summary Disposal facility unpack areas might sustain agent releases, possibly including agents other than the one that its NRT monitors are set up to detect. The Army should analyze whether the addition of real-time and/or multiagent monitoring in those unpack areas that process multiple munitions would significantly reduce risk to workers who unpack and stage munitions for processing. If the risk analysis indicates a significant enhancement of worker safety, the Army should investigate whether other, shorter response time and/or multiagent deployment modes for current NRT monitors or the development and/or procurement of real-time, multiagent monitors based on innovative technology are feasible and practical.

To pose an acute risk to the public, the atmospheric release of sufficient chemical agent vapor or aerosol would require a major accident, almost certainly involving explosion and/or fire. The ability to confirm dispersion model predictions that an agent plume has penetrated the depot boundary and threatens the public or to track the agent plume would require fast-response monitors operating at levels between the STEL and the IDLH that are either widely dispersed or are mounted on a suitable ground or air mobile platform. The Army and other relevant stakeholders should assess whether public protection would be significantly enhanced by the development and deployment of dispersed fixed or portable fast-response agent sensors or the development of a mobile fast-response agent sensor platform capable of detecting and tracking a large release plume.

Open- or folded-path FT-IR and CIMS technology have some promise for providing enhanced, fast-response chemical agent monitoring capability to chemical weapons storage and demilitarization facilities. The Army, however, should only deploy advanced chemical agent monitoring equipment after a thorough risk/benefit analysis shows that the risk reduction to the workforce and/or public justifies the monetary and opportunity costs. If such analyses indicate significant benefit at acceptable cost, systems using FT-IR or, more likely, CIMS should be considered.

For Further Information

Copies of the complete report, *Monitoring at Chemical Agent Disposal Facilities*, can be obtained on the National Academy Press Web <http://books.nap.edu/ >.

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